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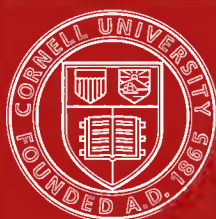


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TWO LECTURES

On The Development and Present Position of Chemical Analysis by Emission Spectra

BY

F. TWYMAN, F.R.S., F. Inst. P.

**LECTURE 1. The Discovery and Development
of Spectrum Analysis.**

**LECTURE 2. (a) Producing, Observing, and
Photographing Spectra.**

**(b) Measuring Wavelengths,
Identifying Metals by their
Emission Spectra, and
Applications.**

PUBLISHED BY

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NOTE.—The 20 lantern slides indicated in the text may be purchased from Adam Hilger, Ltd., for the price of 35/- the set ; or when available may be hired at 5/- per day (postage extra).

PREFACE

THE two lectures in this booklet are based on a lecture delivered before the Sheffield Metallurgical Association, in December, 1924. They are now printed for the use of teachers of Chemistry, etc., with free permission to utilise them in their curriculum.

The publishers have already issued four booklets dealing with spectroscopic analysis. The matter in these booklets is only to a very slight extent duplicated, each of them playing a part in a scheme projected by the author some years ago, the intention of which was to encourage and facilitate the use in industrial laboratories of the spectroscopes and spectrographs made by Adam Hilger, Ltd.

Hilger Instruments in Industry, first published in 1919, and now in its seventh edition, is an alphabetical list of industries in which the instruments referred to are of value. Mention is made of some of the applications, but no details are given.

In *Optical Methods in Control and Research Laboratories*, first published in 1920, Section I. deals with metallurgical and analytical applications of spectroscopy by emission spectra.

Wavelength Tables for Spectrum Analysis, published in 1923, is a compilation of such tables of wavelengths as are daily required in a laboratory where spectroscopy is being employed.

Spectrum Analysis with Hilger Instruments, first published in 1924, is primarily a booklet of instructions for the practice of spectrum analysis, but contains also a note on the modern theory of spectra and further practical applications.

The present booklet, though the latest to be issued, would find its proper chronological place at the commencement of the series, since it deals with the history and development of spectrum analysis.

One further publication, now in preparation, deals in detail with quantitative spectrum analysis, a subject on which much work has been

done recently in the laboratories of Adam Hilger, Ltd. It suffices to state here that where the chemical determination of small percentages of a metal presents difficulties (*e.g.*, cadmium in zinc, calcium in magnesium) a quantitative spectrographic method, rapid and sufficiently accurate, can usually be prescribed.

None of the publications contain descriptions of the instruments; these are best found in the specifications given in the publishers' catalogue, Sections *D*, *E* and *F*

Many readers may find an element of exaggeration in the two sub-headings of Lecture I. ("Period of Suspended Development" and "The Revival of Spectrum Analysis.")

These phrases, however, are well justified. W. Gerlach, writing in the *Zeitschrift für anorganische und allgemeine Chemie*, in February, 1925*, says:

"Merkwürdig vergessen—and besonders gerade in den Kreisen, für die sie geschaffen wurde und heute mehr denn je wichtig ist—, war die chemische Spektralanalyse: Die Analyse einer Substanz nach den von ihr ausgesandten Spektrallinien, wenn sie im dampfförmigen Zustand zum Leuchten gebracht wird. Die auf der Entdeckung Bunsens aufbauenden Pionierarbeiten von de Gramont und von Hartley und einigen anderen Forschern sind jetzt—für Deutschland wenigstens—dankenswerterweise von dem Physiker der Zeisswerke Dr. Löwe, "ausgegraben" worden, während in Frankreich z.B. während des Krieges, in Amerika während der letzten Jahre wichtigste Probleme der Metallforschung mit ihrer Hilfe ihrer Lösung nähergebracht wurden." †

The article by Dr. Löwe, described by Dr. Gerlach as the "ausgegrabung," appeared in the *Z. f. techn. Physik*, 1924. Hartley's publications on the subject commenced in 1882, and Gramont's in 1909. No considerable practical use was made of the results of

* "Zur Frage der richtigen Ausführung und Deutung der 'quantitativen Spektralanalyse,'" von Walter Gerlach, *Zeit. für anorganische und allgemeine Chemie*, Band 142, p. 383, February, 1925.

† This passage may be freely translated:—"Chemical Spectrum Analysis—the analysis of a substance by means of the spectral line it sends out when its vapour is caused to glow—had largely passed out of mind. The pioneer work which A. de Gramont, Sir W. N. Hartley, and several other workers founded on Bunsen's discovery has now been "exhumed"—at least as far as Germany is concerned—by Dr. Löwe, the physicist of the Zeiss Works; while in France, for example, during the War, and in America in the last few years, most important problems in Metallurgy have by its aid been brought nearer to solution."

Hartley, Pollok, Leonard and Gramont before the instruments designed by the present writer came on the market in 1904 (wavelength spectrometer) and 1909 (fixed adjustment quartz spectrographs); but from the latter date till 1914 many important chemical laboratories in all parts of the world (including Germany) were equipped with these instruments; while since 1918 their adoption has been rapid. Thus, although the date of the revival of chemical analysis has been placed somewhat late by Dr. Gerlach, the fact that the subject seemed to him to require "exhuming" in 1924 shews how completely the method had gone out of general use.

In conclusion, as has been pointed out by Schuster, the term "Spectrum Analysis" is sometimes applied to the separation of the spectrum into its constituent homogeneous radiations. In this booklet, the word denotes, as originally, the use of the spectroscope or spectrograph to identify the constituents of a chemical compound by the radiation emitted under the action of either heat or electric current. It would be very natural to extend the use of the phrase to cover similar analysis by observation of absorption spectra or of fluorescence spectra.*

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* For example, the fluorescent response of a substance when a spectrum is projected upon it (see S. Judd Lewis, *Journ. Soc. Dyers and Colourists* 1918, 1922 and 1924).

LECTURE I.

THE SPECTROSCOPE AND SPECTROGRAPH

The Early History of Spectrum Analysis.

The early steps in the development of spectrum analysis are summarised in the two first lantern slides.

PUBLICATIONS OF PRIME IMPORTANCE IN THE HISTORY OF SPECTRUM ANALYSIS, 1672 to 1817

- 1672 Discovery of the dispersion of light. (*Newton.*)
- 1800 All parts of the spectrum have power to heat bodies including an invisible extension of the spectrum beyond the red end. (*W. Herschel.*)
- 1801 The power of light to blacken silver chloride is possessed also by an invisible extension of the spectrum beyond the violet end. (*Ritter.*)
- 1802 Application of the wave theory of light to explain the diffraction of light by gratings, and first determination of the wavelengths of various colours by Newton's rings. (*Thomas Young.*)
- 1802 First observation of absorption regions in the sun spectrum and of a discontinuous emission spectrum. (*Wollaston.*)
- 1817 Construction of the first spectroscope and its use for the first observation of metallic emission lines (the yellow doublet of sodium). First measurement of the lines of the solar spectrum, and first observation of the spectrum of a star. Measurement of the refractive indices of various glasses for the principal lines of the solar spectrum. First observation of the spectrum of the electric spark. (*Fraunhofer.*)

LANTERN SLIDE NO. 1.

THE PERIOD OF SUSPENDED DEVELOPMENT.

We see that already in 1861, there was available a not inefficient spectroscope, a knowledge of how to produce the spectra of substances and of how to interpret them as evidence of the presence of metals.

It is noteworthy that when Kirchhoff and Bunsen communicated their great discovery, they called the production and examination of spectra—"Spectral Analyse"—*spectrum analysis*, and not *spectroscopy*. The use of this method had in particular cases a brilliant success, as the discovery of numerous new elements witnesses, but although spectrum analysis became one of the customary operations in the laboratory of Bunsen as a new aid in qualitative analysis, and although, since that time there have always been a few workers who had constant recourse to

PUBLICATIONS OF PRIME IMPORTANCE IN THE HISTORY
OF SPECTRUM ANALYSIS, 1821 TO 1861

- 1821 Invention of the diffraction grating as a means of producing spectra, and measurement therewith of the wavelengths of the solar lines thereafter called Fraunhofer lines. (*Fraunhofer.*)
- 1823 First systematic observations of metallic emission spectra, and attempt to record their positions graphically. (*J. F. W. Herschel.*)
- 1852 Experiments leading to the conclusion that the original light from the sun forms a continuous spectrum, and that the dark Fraunhofer lines are due to the vapours surrounding the sun. (*Brewster.*)
- 1835 Spectrum analysis of lithium and strontium. (*W. H. F. Talbot.*)
- 1835 Drawings of the spark spectra of Na, Hg, Zn, Cd, Bi, Sn, Pb. (*Wheatstone.*)
- 1842 The first photographs of a spectrum (the solar spectrum)—on a daguerrotype plate. (*Becquerel and Draper independently.*)
- 1855 The spectrum of a spark discharge between metallic electrodes is distinctive of the metal. Drawings of the spark spectra of many metals and some alloys. (*Ångström.*)
- 1861 Discovery that the vapour of a metal produces absorption lines identical in position with the emission lines of its flame spectrum. The first spectrometer, and the first use of a collimator. (*Kirchhoff and Bunsen.*)

LANTERN SLIDE No. 2.

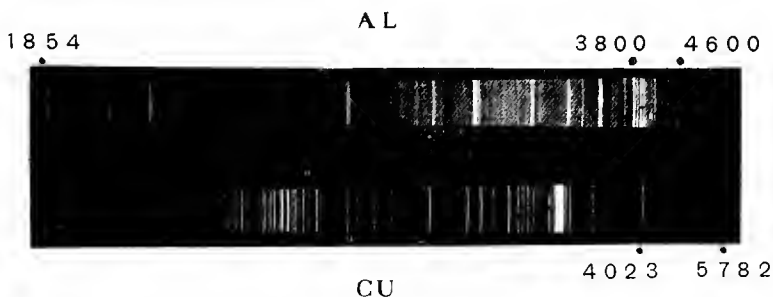
the spectroscope in their daily work, yet seventeen years ago the original expectation that the new method would immediately find use as a general method of qualitative analysis had been lost sight of to such an extent that the majority of chemists scarcely ever used a spectroscope at all.

There were numerous reasons for this. First may be mentioned the extraordinary sensitiveness of the method. Unless one takes the

utmost care it is impossible to get rid of the two yellow lines of sodium, whatever substance one is examining and this is only an extreme case of what often happens in spectroscopy. Thus, in many cases spectrum lines would shew in which the chemist had, at that time, no interest.

Again in the use of a particular spectroscopic routine it was only certain of the elements that shewed this extraordinary sensitiveness, others scarcely revealing their presence.

For instance, in the Bunsen flame, only the alkali metals shew with intensity. The alkali earth metals, with the addition of indium and thallium show feebly, while the other metals do not show at all. It is true, that it was known quite early that metals in general in the spark revealed their presence by their characteristic spectra, but convenient means of providing electric current were not, in the years immediately following 1861, generally available.



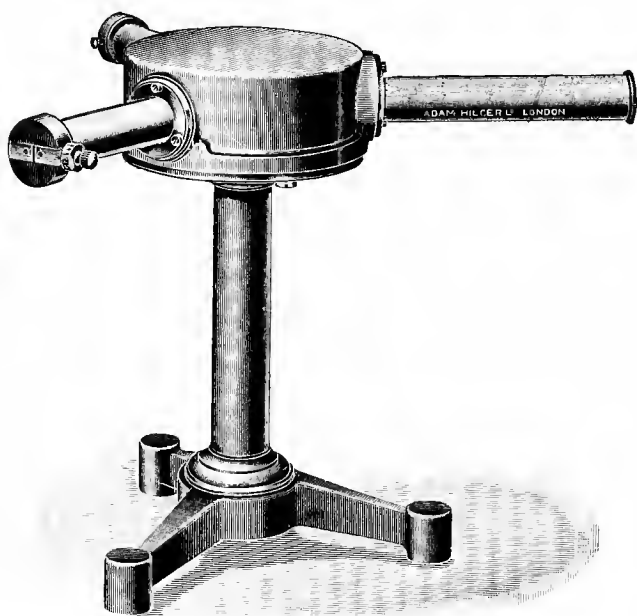
LANTERN SLIDE NO. 3

When the spark and arc spectra became available by the extension of electrical facilities, there was a third deterrent to the use of the spectro-scope, for many of the elements gave spectra very rich in lines, and little characteristic to a casual glance. The unravelling of such a maze of lines might well seem more difficult and tedious than the full routine of chemical analysis. Again there was no known quantitative relation between the appearance of the lines of a metal and the percentage present in the substance examined.

Everyone will appreciate the importance of such a permanent record as a spectrogram (that is, a photographed spectrum) affords. But there is another advantage possessed by a spectrograph. A glance at lantern slide No. 3 will shew what a valuable region is excluded if one has a visual instrument as compared with a quartz spectrograph. Wavelength 4023 represents about the extreme of the visible violet, the region from 3800 to 1854 being invisible.

Photography has now become so familiar to everyone that its employment as a laboratory routine is customary ; but thirty years ago, this was not the case and there is no suitable means,* other than photography, of observing or recording the ultra-violet spectrum which is so valuable in spectrum analysis.

In 1893 Rowland published his first *New Tables of Standard Wavelengths*, which gave, for the first time, the wavelengths of reference lines with the accuracy needed for analysis of substances which have complex spectra ; but it was not till a good deal later that tables of the wavelengths of the elements became readily available.†



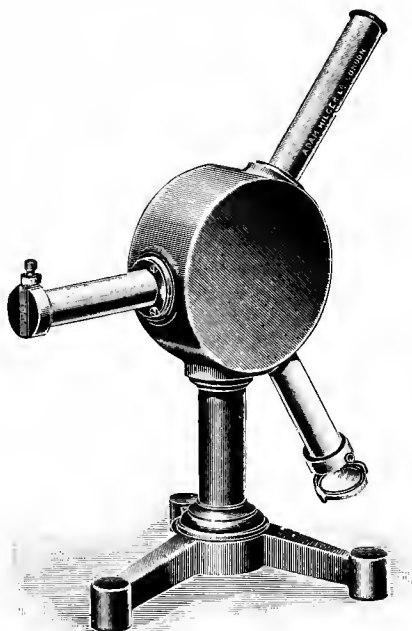
LANTERN SLIDE NO. 4.

* The ultra-violet spectrum can be made visible by fluorescence, or explored by the thermopile, bolometer, selenium detector, or photoelectric cell. Particulars of instruments for such work will be found in section D of the publishers' catalogue, but they are not suitable for spectrum analysis.

† Particulars of the units in which wavelengths of light are stated for the purposes of spectroscopy will be found in *Wavelength Tables for Spectrum Analysis*, see page 45.

Perhaps, however, the most potent reason why the chemist avoided spectroscopy was the lack of a suitable apparatus.

All the more customary flame examinations can be performed with the very simplest of instruments. There are shewn in lantern slides Nos. 4 and 4A, two modern equivalents of the Bunsen and Kirchoff spectroscope, differing from the latter only in being more solidly designed and in having a wavelength scale instead of the original arbitrary scale. Such an instrument is excellent for the detection of the alkali metals by their flame spectra, but is of little use for general metallurgical work.



LANTERN SLIDE NO. 4A.

Thus, although spectroscopy developed, it was mainly under the auspices of the physicist and the astronomer. For these it rapidly became an instrument of supreme importance, but in the academic laboratories it was chiefly used, if at all, as a means of teaching optics, and instruments were deliberately made with as many adjustments as possible in order that the students might learn the principles of the instrument rather than its use as an implement of research.

Thus, the busy chemist who bought a spectroscope was chiefly solicitous that it could be put away in a case and that the case should be as small as possible.

These are the obstacles which delayed the general adoption of spectrum analysis.

DISTINCTIVE LINES OF THE ELEMENTS

(*from "Wavelength Tables for spectrum analysis."*)

Index of elements whose persistent lines are given in the tables of Hartley, Pollok and Leonard, on pp. 26 to 63. The chemical symbols are here arranged alphabetically. The elements whose sensitive rays are given by A. de Gramont are arranged alphabetically on pp. 81 to 84.

SYMBOL.	ELEMENT.	PAGE.
Ag	Silver	31
Al	Aluminium	28, 42
As	Arsenic	33
Au	Gold	66
Ba	Barium	46
Bi	Bismuth	34
Ca	Calcium	47
Cd	Cadmium	28
Ce	Cerium	50
Co	Cobalt	45
Cr	Chromium	43
Cs	Caesium	65
Cu	Copper	30
Fe	Iron	42
Hg	Mercury	32
In	Indium	29

LANTERN SLIDE No. 5.

In connection with the application of the spectrograph to chemical analysis and metallurgy, the following extract is interesting :

"The application of modern physical ideas to the study of metals is most fascinating, and whilst the results may often seem to the practical man to be of purely academic interest, nothing is more certain than that the academic knowledge of today will profoundly affect the industrial practice of tomorrow."

C. H. Desch. (*Physics in Industry*, Vol. II, Lecture VI, "The Physicist in Metallurgy.")

The Revival of Spectrum Analysis.

The resuscitation of spectrum analysis is to be referred primarily to two workers—W. N. Hartley (with his assistants) and A. de Gramont.

* Hartley, working at the University of Dublin, first noted that it is not always the strongest lines of an element which are the most persistent

SYMBOL.	ELEMENT.	PAGE.
K	Potassium	48
La	Lanthanum	51
Li	Lithium	64
Mg	Magnesium	26, 48
Mn	Manganese	44
Mo	Molybdenum	54
Na	Sodium	49
Nd	Neodymium	53
Ni	Nickel	45
Pb	Lead	33
Pr	Praseodymium	53
Rb	Rubidium	65
Sb	Antimony	34
Si	Silicon	43
Sn	Tin	32
Sr	Strontium	47
Te	Tellurium	33
Th	Thorium	56
Ti	Titanium	59 and 60
Tl	Thallium	29
U	Uranium	61
V	Vanadium	62
W	Tungsten	55
Y	Yttrium	52
Zn	Zinc	27, 44
Zr	Zirconium	57

LANTERN SLIDE NO. 5A.

when that element is present in a substance in small and decreasing amounts. Already in 1882, he had investigated the proportions of certain metals which would be evidenced in compounds by the presence of their lines in the spectrum, and had as a result, estimated the amount of beryllium contained in certain cerium compounds. He preferred to work with solutions, and used the spark condensed by a Leyden jar.

* Full bibliographies of the publications on the work of Hartley, Pollok, Leonard and A. de Gramont will be found in *Wavelength Tables for Spectrum Analysis*, by the present writer (Adam Hilger, Ltd.). A note on the modern theory of emission spectra, which partly explains the observations of Hartley, Pollok, Leonard and A. de Gramont, will be found in *Spectrum Analysis with Hilger Instruments*.

Hartley's work was continued, also at Dublin, by Pollok and Leonard, and this group of workers studied the metals named in the next two lantern slides, 5 and 5A.

Pollok and Leonard distinguished the lines of each particular metal by Greek letters, which shew the persistence of the spectrum line as the quantity of metal present was reduced (see slides 6 and 7).

(POLLOK'S NOMENCLATURE FOR THE SENSITIVE SPECTRUM LINES OF METALS IN SOLUTION AS PHOTOGRAPHED ON A HILGER QUARTZ SPECTROGRAPH.)

To distinguish briefly between the different phases of the lines, with diminishing concentration, use has been made of some of the letters of the Greek alphabet, with the following meanings :

- τ = seen with the metal, but not with strong solutions.
- σ = seen with strong solutions, but not with 1% solutions.
- ϕ = seen with 1% solutions, but not with .1% solutions.
- χ = seen with .1% solutions, but not with .01% solutions.
- ψ = seen with .01% solutions, but not with .001% solutions.
- ω = seen with .001% solutions.

LANTERN SLIDE No. 6.

The above Table appears in "Wavelength Tables," page 41.

In this way Hartley and his co-workers laid the basis of an approximate quantitative spectrum analysis and although it is only in rare cases that this method can compare with the balance it provides a means of readily distinguishing between a considerable percentage of a material and mere traces only, which is often very valuable. More important still, it is now unnecessary in hunting for a small quantity of a substance in a sample to look for any but the few lines known to be persistent.

The work of A. de Gramont working at the Sorbonne was of a similar character, and he also used the condensed spark, but he worked chiefly with solids.

All these observers agree on the importance of noting those lines which are still shewn when an element is present in a substance in very feeble quantity. These are called by Hartley, Pollok and Leonard, "distinctive lines." Gramont called them "Raies sensibles," while those remaining last of all when the amount is decreased he called "Raies Ultimes." These rays present the following characteristics :

1. They are not necessarily the strongest lines in the spark spectrum of the element.

2. They are present in the spark, but belong to the arc spectrum of the element, where they are generally of great intensity.

3. They are generally present also in the spectra of very hot flames (oxyhydrogen or oxyacetylene).

A number of Gramont's lines are given in lantern slide No. 7.

QUANTITATIVE SPECTRUM OF COBALT CHLORIDE			
WAVELENGTH.	INTENSITY AND PERSISTENCY.	WAVELENGTH.	INTENSITY AND PERSISTENCY.
4531.1	4σ	3412.8	7φ
10		3405.3	8ψ
4469.7	1σ	15-17	
4121.5	8φ	3086.9	6φ
4118.9	8σ	3072.5	6φ
12		18-21	
3995.5	8φ	2694.7	8ω
13		22	
3894.2	10ψ	2663.6	8χ
3873.2	10ψ	23-24	
3845.6	10φ	2587.2	8φ
14		2582.3	8χ
3502.4	8χ	2580.4	8ψ
3489.5	10φ	2564.2	8φ
3474.1	10χ	2559.5	8χ
3465.9	8φ	25	
3453.6	8ψ	2528.7	7χ
3449.6	7φ	2525.1	7χ
3443.8	7φ	2519.0	8ω
3433.2	7φ		

LANTERN SLIDE No. 6A.

The above Table appears in "Wavelength Tables," page 45.

A. de Gramont found these conclusions hold for alloys, minerals, and fused salts, and states that his observations are in general agreement with those of Pollok and Leonard in the case of solutions, which greatly increases the value of the tables of all these observers.

But Hartley, Pollok and Leonard give lines which Gramont omits in his summary, and vice versa ; thus it is wise to refer to the tables of both sets of workers. Gramont, for instance, in his summary omits among others the useful nickel lines 3050.9 and 3054.4

RAIES DE GRANDE SENSIBILITÉ ET RAIES ULTIMES DES ÉLÉMENTS

ALL THESE WAVELENGTHS ARE IN INTERNATIONAL ANGSTROMS.

Par la photographie :

Symbol.	<i>A l'observation oculaire :</i>	<i>Par la photographie :</i>	
		Spectrographe <i>crown uiol.</i>	Spectrographe <i>quartz.</i>
Mo	5570,5 ; 5533,2 ; 5506,5..	3903,0 _u (1) ; 3864,1 _n ; 3798,3 _n (1) ; 3635,2	
Nd	4303,6 ; 4177,3 ; 3951,2	
Ne	3619,4 ; 3524,5 ; 3515,1 ; 3414,8 _n ; 3380,6	2437,9 ; 2416,2 _n ; 2316,1 _u ; 2303,0 _n
Ni	5476,9 ; 5081,1 ; 4714,4	2802,2 ; 2676,0 _n ; 2428,0 _n
Au	6278,2 ; 5837,4 ; 4792,6..	
Os	3634,7 _n ; 3609,6 _n ; 3421,2 ; 3404,6 _n	2555,0 ; 2553,3 _n ; 2535,6 _n ; 2534,0
O	5547,0 ; 5295,6 ; 5163,8	3064,7 ; 2929,8 ; 2659,4
Pd	3966,4 _n ; 3923,0 ; 3268,4.....	
P	5475,8 ; 5390,8 ; 5301,0 ; 5227,6	2614,2 ; 2203,6 ; 2175,8
Pt	4057,8 _{n1} ; 3683,5 _{u2} ; 3639,6	
Pb	5608,9 ; 5005,5	4047,2 _{n1} ; 4044,2 _n ; 3447,4 ; 3446,4	
K	7699,0 ; 7669,4 ; 5832,0 ; 5801,8 ; 5782,4	(4825,9 ; 4682,2 ; 3814,5) (2)	
Pr	3799,3 ; 3692,4 ; 3658,0 ; 3434,9 _n	
Ra	4215,6 _{u2} ; 4201,8 _{n1}	
Rh	7947,6 ; 7800,3	3499,0 _n ; 3436,7	
Rb	4246,9 ; 3651,9 ; 3630,8 _n ; 3613,8 _{n1}	
Ru	3905,5	2881,6 _n ; 2528,5 ; 2516,1 _u ; 2506,9
Sa	6370,9 ; 6346,8.....		
Sc		
Se		
Si		

[1] Non étudiés par l'auteur.

[3] En cours d'étude ; résultats provisoires.

(1) Masquées par des raies du fer.

[2] Ne donnant ni raies ultimes ni raies de grande sensibilité.

[4] Étudiés seulement au crown uiol ; résultats provisoires.

(2) Runge et Precht.

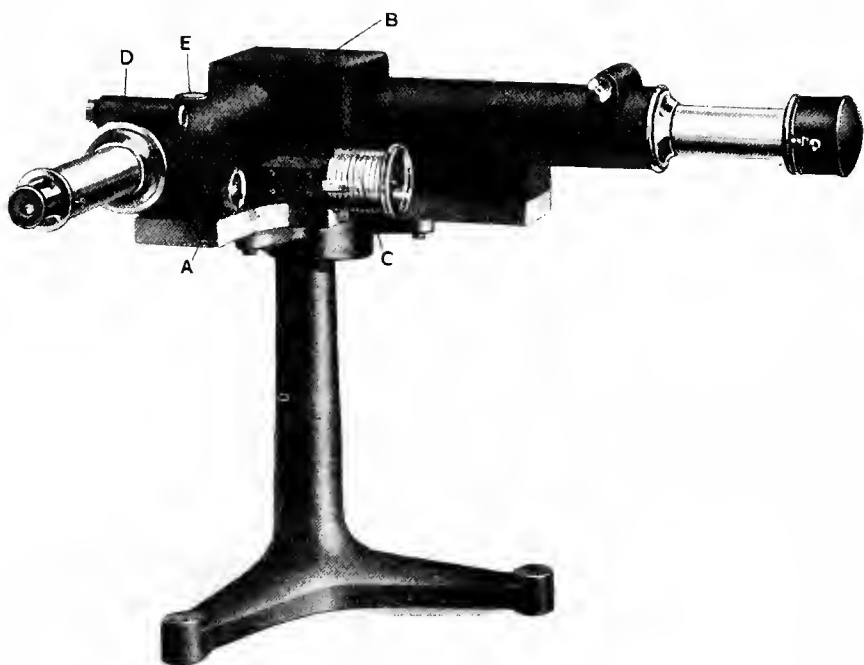
FROM "WAVELENGTH TABLES FOR SPECTRUM ANALYSIS"

RESEARCH DEPARTMENT,

ADAM HILGER, LIMITED.

The order of sensibility is that found by photography, either with a quartz or with a uviol crown glass spectrograph, and it is in the ultra-violet that the "Raies Ultimes" almost always lie. But where "raies sensibles" are recorded in the visible spectrum they are often of high sensibility for the eye.

The instruments with which Hartley and Gramont worked in the first instance, although quartz spectrographs, were not of the modern convenient kind and entailed manipulations of a nature not generally familiar.



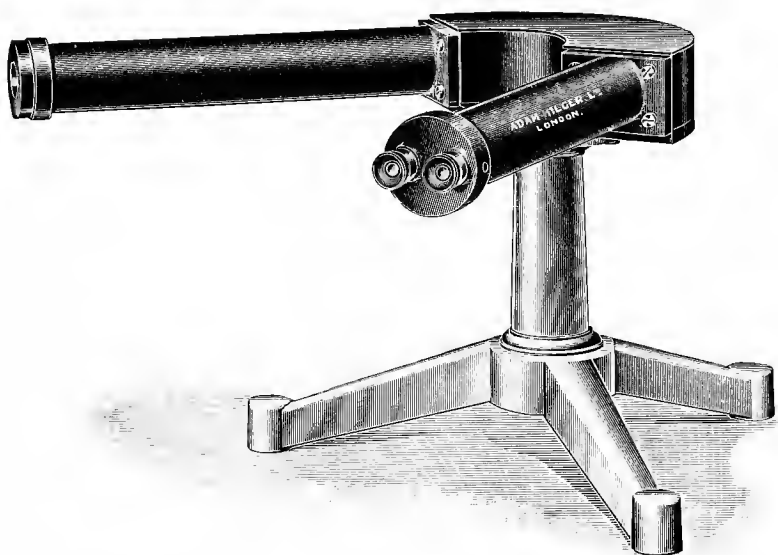
LANTERN SLIDE NO. 8.

MODERN APPARATUS FOR SPECTRUM ANALYSIS.

In 1904 the author became strongly conscious of the need for more convenient and labour saving spectroscopes, and in that year utilised the form of prism already made known by M. Broca, to design for the firm of Adam Hilger, the now well-known Wavelength Spectrometer. This was a visual instrument in which there was no divided circle, the

telescope and collimator being fixed and the prism rotated by a micrometer screw on the large head of which wavelengths of the line under observation were engraved. It is shewn in slide No. 8—it is made in three sizes.

With a large wavelength spectrometer an observer can state almost at a glance which of the metals most frequently used in steels are present. He can also guess the quantities present with sufficient accuracy for many purposes—this is the case with Ni, Co, Cr, W, Mo and Va, and in all probability with Mn, Cu, and Ti, although these have not been investigated with like care.



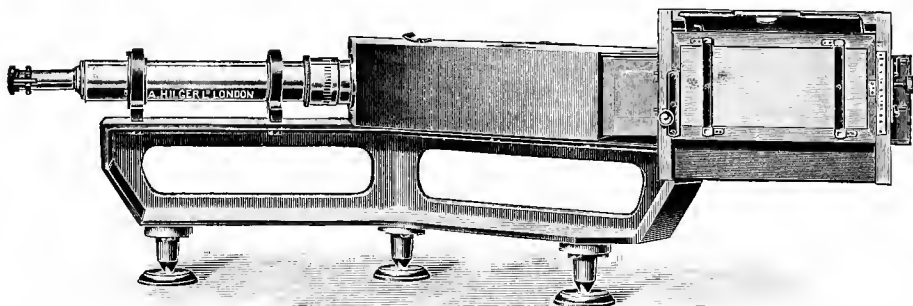
LANTERN SLIDE NO. 9.

As an example of what can be done in this direction, mention may be made of the specialised form of spectroscopes made for the visual detection of Ni, Cr, Mo and Va in steels.

One of these instruments, designed for testing bars in the rolling mill or warehouse, shewn in slide 9, consists of a substantial casting, the two screw-focussing eye-pieces at the one end and a stout protective glass plate at the other, so that it is effectively protected not only against damage but against all liability to go out of adjustment. The method of use is extremely simple :

A bar of Carbon steel is held in a suitable wooden frame and the bars to be tested are then placed in position on V-supports one by one as rapidly as possible, connection with the electric mains being provided through a suitable resistance giving about 5 amperes. Direct current of from 150 to 250 Volts is necessary.

The arc is struck by touching both rods simultaneously with a third rod of Iron or Carbon steel (insulated by pushing over one end of it a piece of ordinary rubber tube). Removal of this rod strikes the arc, and the observer at the spectroscope is able to state whether or no the sample contains an important quantity of Nickel or Chromium. With the aid of three or four standard samples containing various percentages of Nickel and Chromium, he can soon accustom himself to state also the range of percentage within which the Nickel or Chromium content lies.



LANTERN SLIDE No. 10.

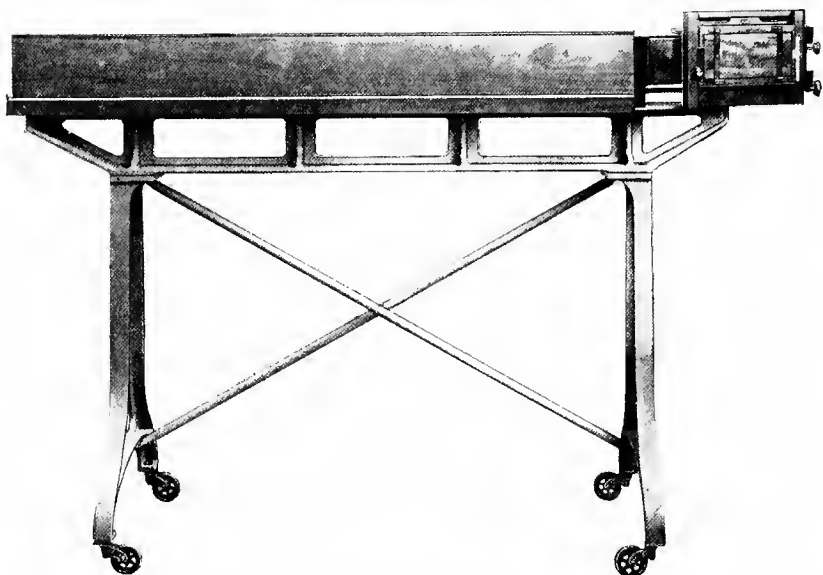
Several of these instruments have been in use by Messrs. Vickers works at Sheffield for over two years, and they report :

“ The Spectrograph supplied by Adam Hilger Ltd., has now been in constant daily use in the Steel Warehouse for nearly twelve months and has proved a most useful check in the detection of mixing in bars. The operators have now reached a state of efficiency sufficiently high to detect bars of wrong quality in a batch with almost unfailing accuracy, and it is possible to state that the presence of chromium or nickel can be definitely detected when 0.1% of chromium or 0.5% nickel is present. We find it comparatively simple to differentiate by Spectroscope between steels containing, for instance, the following amounts of nickel and chromium :

- “ (1) A carbon steel containing less than 0.5% nickel and one containing 1% nickel.
- “ (2) Case-hardening nickel steels containing 2%, 3% or 5% of nickel.
- “ (3) A 3% nickel steel from a 3% nickel chrome steel.
- “ (4) Nickel chrome steels containing 0.5%, 1% or 1.5% chromium respectively.

" The Spectroscope is also used in this Department to determine the quality of scrap selected at random from the bins of other Depts., and it is found quite possible to say whether a piece of steel is carbon scrap or nickel scrap.

" We find that the time taken to carry out a spectroscopic observation is about thirty seconds to a minute when testing a batch of light bars of the same size and quality—heavier bars, of course, require more handling and cannot be dealt with quite so expeditiously."



LANTERN SLIDE No. 11.

So much for visual instruments. But as the work done by Gramont, Hartley, Pollok and Leonard was published, it became obvious that for general use a convenient photographic instrument was needed, and in 1909, the author designed the fixed adjustment quartz spectrograph which, with slight modifications, is the same as that shewn in slide No. 10.

In 1912, in order to deal more readily with the very complex spectra of modern steels, a still larger size quartz spectrograph (now known as E. 1) was made, giving three times the dispersion of the former one (see Slide 11).

All of you who have taken any interest in spectrography will, of course, know of the diffraction grating. You will read in all the text

books of the superiority of the diffraction grating over the prism owing to its high dispersion and its normal spectrum.

It may, therefore, interest you to see a comparison between spectra taken with a grating spectrograph and a quartz spectrograph. Lantern slide 11A shews grating and quartz prism spectra, both of exactly the same range of spectra, and a particular wavelength has been marked on each.

You will see that the prism spectrum is relatively short towards the long wavelengths, and relatively long towards the short wavelengths. The grating spectrograph is widely used in physical laboratories, but it is not so generally suitable for spectrum analysis owing chiefly to the comparatively long exposures which require to be given.

GRATING AND QUARTZ PRISM SPECTRA
OF COPPER ARC COMPARED



RESEARCH DEPARTMENT ADAM HILGER LIMITED

LANTERN SLIDE NO. 11A.

The constructions of these two quartz spectrographs are illustrated in Lantern Slide No. 12.

Diffraction gratings are now being ruled regularly by the National Physical Laboratory, on a ruling engine the construction of which was commenced in the Laboratory of Lord Blythswood by the late Mr. Otto Hilger, afterwards the proprietor and manager of the firm which is now incorporated as Adam Hilger, Limited.

You will have noticed that A. de Gramont mentions two instruments, the quartz spectrograph and the uvioi spectrograph.

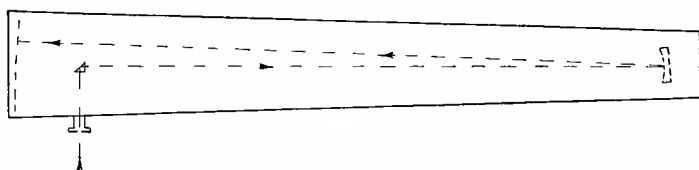
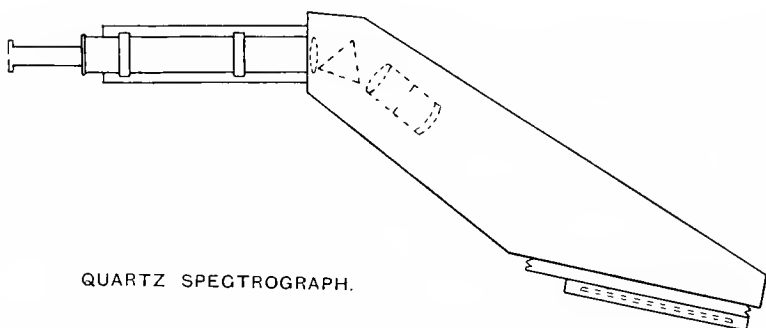
The uviolet spectrograph has a large dispersion and is very suitable for use with steels and ferrous alloys. Although it does not reach so far in the ultra-violet as the quartz spectrograph, it yields distinctive lines of most, if not all metals, I think, which are of interest in steels or ferrous alloys.

Lantern slide No. 13 shews the sensitive lines which are to be found in the ranges of the two instruments.

AUXILIARY APPARATUS.

Scarcely less important than a suitable spectrograph are convenient auxiliary apparatus and a well considered routine of work suitable for the daily problems of the metallurgist.

The number of spectroscopic accessories which have been devised probably run into many hundreds. I shall mention in the next lecture some that are most useful for the spectrum analysis of metals and salts.



METALS			
With Ultimate Spectrum Lines lying within the Range of the Quartz Spectrograph E. 3 and of the Uviol Spectrograph E. 42.			
UVIOL SPECTRO- GRAPH.	QUARTZ SPECTRO- GRAPH.	UVIOL SPECTROGRAPH.	QUARTZ SPECTROGRAPH.
Aluminium	Aluminium	Manganese	Manganese
—	Antimony	—	Mercury
Silver	Silver	Molybdenum	Molybdenum
—	Arsenic	Nickel	Nickel
Barium	Barium	—	Gold
—	Bismuth	Palladium	Palladium
—	Boron	—	Phosphorous
—	Cadmium	Platinum	Platinum
Caesium	Caesium	Lead	Lead
Calcium	Calcium	Potassium	Potassium
—	Carbon	Rhodium	Rhodium
Cerium	Cerium	Rubidium	Rubidium
Chromium	Chromium	Ruthenium	Ruthenium
Cobalt	Cobalt	Scandium	Scandium
Niobium	Niobium	—	Silicon
Copper	Copper	Sodium	Sodium
Tin	Tin	Strontium	Strontium
—	Iron	Tantalum	Tantalum
Gallium	Gallium	—	Tellurium
Germanium	Germanium	Thallium	Thallium
—	Beryllium	Titanium	Titanium
Indium	Indium	Tungsten	Tungsten
Iridium	Iridium	Neo-Ytterbium	Neo-Ytterbium
Lanthanum	Lanthanum	Yttrium	Yttrium
Lithium	Lithium	Zinc	Zinc
—	Lutecium	Zirconium	Zirconium
—	Magnesium	—	—

LANTERN SLIDE No. 13.

Taken from the results of Gramont as appearing in "Wavelength Tables for Spectrum Analysis."

LECTURE II.

PRODUCING, OBSERVING AND PHOTOGRAPHING SPECTRA

LIGHT SOURCE.

There are four main ways of producing from a substance radiation suitable for its spectroscopic analysis: by the flame, the arc discharge, the spark discharge, and the vacuum tube discharge.

In the flame it is only certain metals which emit radiations capable of analytical interpretation. In the arc all the metals and in addition the five non-metals, carbon, silicon, boron, phosphorus and arsenic, reveal their presence by characteristic spectra. In the spark, the scope is still wider, for many of the non-metals, among them fluorine, chlorine, bromine, iodine, oxygen, nitrogen, sulphur and selenium, become detectable as well as the metals, and the method is applicable to solutions as well as solids, which is not the case with the arc.* With the spark "air lines" † are usually in evidence, but these can be removed by the use of a self-induction coil.

Under ordinary conditions in the vacuum tube the substance of the electrodes gives no spectrum, the lines present being only those of the rarefied gas in which the discharge takes place.

The wavelengths of the spectrum of a metal are not affected either by its state of chemical combination, or by the presence of other metals.

Flame Spectra.

Every chemist is familiar with the production of flame spectra. They are obtainable from certain metals or their salts when these are put into a Bunsen flame. A small quantity of the substance, or of a strong solution of it, is gathered on a loop at the end of a platinum wire, and introduced into the outer part of the flame near its base.

* The last named eight elements do not, however, give their spectra under such conditions as to render their spectroscopic detection in a substance generally feasible.

† *i.e.* lines of oxygen and nitrogen.

Innumerable variants of this device are to be found in the mass of literature which has accumulated since the time of Bunsen, who originated this method in 1859, but it suffices to state here that as far as analytical purposes are concerned :

- (a) Flame spectra are of value only in identifying the alkali and alkaline earth metals with the addition of indium and thallium ;
- (b) A spectroscope of low dispersion and high luminosity is the best ;
- (c) The ultra-violet spectrum in flame spectra being too weak to have any value for analysis, a visual spectroscope is all that is required ;
- (d) Although in the case of sodium the phenomenon lasts a considerable time, yet in other cases such as those of potassium and rubidium it is very evanescent and the observation should therefore be made at the instant of introducing the salt into the flame.

When attempting to detect the presence of extremely small quantities of potassium, rubidium, etc., the procedure of Gooch and Phinney may be adopted.*

Arc Spectra.

Arc spectra are I think, the most generally useful, and when electric supply at from 150 to 220 volts D.C. is available the production of the arc between metal electrodes is very simple.

When the voltage available is less than this, or when A.C. only is available most metallic arcs will not run ; but the difficulty may be avoided by using carbon electrodes, and putting the substance to be examined on the lower pole.

A simple hand feed holder is connected to the supply through a resistance, a current of from 3 to 6 amperes being used. Electrodes, as pure as possible, of carbon, copper or iron, or of the metal to be examined, are held in the holder, and the arc is struck by allowing the electrodes to touch and then separating them by two or three millimetres. The following procedures suffice for practically all cases likely to arise.

Metallic specimens. Where the specimen is in the form of metallic rods or metallic pieces large enough, these can themselves be used as electrodes.

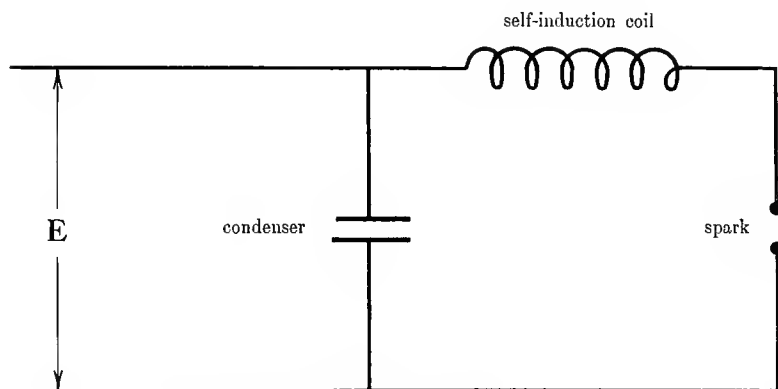
* *Am. Journ. Sci.*, vol. 44, p. 392. " The Quantitative Determination of Rubidium by the Spectroscope."

Small metallic or other specimens, powders, precipitates, dry residues from solutions, etc. Carbon electrodes are used, and a small cup is scooped out in the lower carbon. Into this the specimen is dropped and the arc struck. A variant of this procedure is to use copper electrodes, a few milligrams of the substance being placed on the lower copper pole when the latter is hot. The substance adheres to the pole, and the spectrum of its metallic components is observable for some time.

Spark Spectra.

The apparatus required for producing the spark consists of an induction coil, or preferably, a small transformer giving 15,000 volts on open circuit, with a condenser and self-induction coil. If alternating current is not available, a small converter must be added.

These are arranged as in Slide 14.



LANTERN SLIDE No. 14.

Solids, including powders. The specimens for sparking are held in clips in an adjustable holder. This holder suffices for metals, alloys or conducting minerals. If the specimens consist of non-conducting powders (such as those of slags, precious stones, stony minerals, glasses, precipitates or residues from solutions), there should be added a small cup of platinum about 20 mm. diameter and 5 mm. deep, held in the lower clamp by a wire of the same metal, the cup being heated in the flame of a Meker burner. A stout platinum wire leads the spark from the upper clamp to the platinum cup, in which the powder or powdered mineral is mixed and fused with about four times its weight of sodium or lithium

carbonate—these salts being chosen because of the simplicity of their spectra.

Liquids. If the samples are in the form of solutions, the sparking tubes of Hartley or of Pollok may be adopted.

Great weight has been attached by several of the most important workers on spectrum analysis to the superior advantages of the spark. In the experience of the author where metals alone are concerned, the arc is generally as good as the spark ; indeed, it is usually superior not only in convenience but in sensitiveness. Although Hartley, Pollok and A. de Gramont worked exclusively with the spark, their results are widely applicable to the arc, for lines which are sensitive or persistent in the spark are generally sensitive also in the arc, though the order of sensitiveness with the arc does not appear to be always the same as with the spark.

But there are certainly some cases where a metallic impurity shows in smaller quantity with a spark than it does with an arc. After all, if a metal of high melting point is present in small amount in one of low melting point, there is not likely to be a large proportion of the former in the vapours from which the spectrum is derived. If we add to this that the ionisation potential of the former metal may be high and the voltage of the arc low (and all these conditions are liable to occur together), it becomes natural to guess that the spark with its higher voltage and disruptive, rather than volatilising, provision of glowing vapour, should be more sensitive in its detection of the impurity.

Data on which accurate correlation could be based are lacking—but with the above considerations in mind an intelligent guess can be made as to when the spark should be tried.

The condensed spark will also bring out lines not only of the metals, but of many of the non-metals as well, though with the exception of the metalloids tellurium, phosphorus, arsenic, antimony, carbon, silicon, boron, which A. de Gramont found in fused salts, minerals and alloys, little practical use has been made of this in spectrum analysis.

CONDENSER.

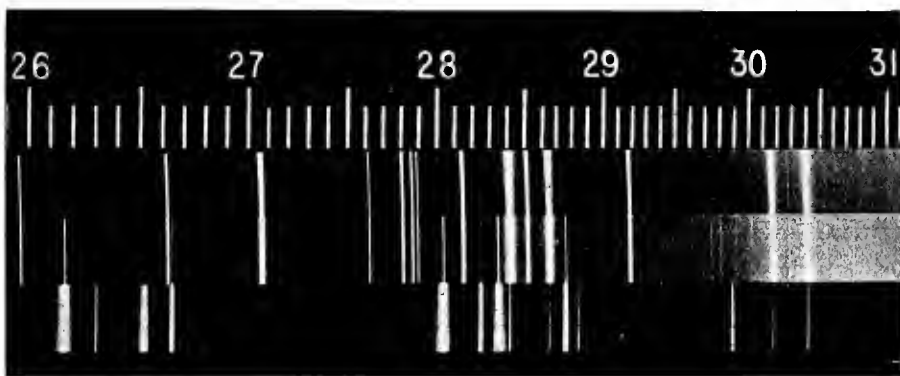
So much for the light source. Next in order comes the condenser by which an image of the light source is thrown on the slit of the spectrograph.

It is usual to employ a condenser of the “ Sphero-cylindrical ” type, which throws a line of light on the screen. This has its advantages, producing as it does a spectrum in which the intensity of each line is uniform from top to bottom ; but the discrimination between the “ long ”

and "short" lines of Lockyer is thereby lost, and it is probable that, now that the significance of these lines is better understood there will be a reversion to the use of the spherical condenser.*

COMPARISON SPECTRA.

Here is a slide, No. 15, in which the spectra of several samples are shewn close together. These spectra are taken one after the other on the same plate without any readjustment of the spectrograph. If there are any constituents common to two or more of the samples the spectrum lines of those constituents will appear in the corresponding spectra. Spectra so arranged are called "Comparison Spectra." The best method of producing them in spectrum photography is by what is known as the Hartmann Diaphragm.



LANTERN SLIDE NO. 15.

The Hartmann Diaphragm consists of a sliding plate with several holes, usually three, any one of which can be brought in front of the slit. With the bottom hole in position a spectrogram of one specimen is taken. Without moving the dark slide or shutter of the camera and with the middle hole in position, a spectrogram of the next specimen is taken; and so with the third.

*The "long" lines of Lockyer have been identified with the sensitive rays of A. de Gramont.

MEANS OF IDENTIFYING THE LINES.

The questions the chemist may refer to the spectrograph are broadly divisible into two classes :

- (1) Does a given substance contain this, that or the other metal ?
- (2) What are all the metals present in this substance ?

We shall consider a suitable procedure for each of these two cases.

(1) *To ascertain whether a Substance contains a Specified Metal.*

Using the Hartmann Diaphragm as described above, one takes three spectra, of which the first is that of any metal which is known to be present in considerable quantity, or if none such be known then one of the purest iron obtainable ; the second that of the sample under test ; while the third is that of the metal whose presence or absence is to be determined.

The set of photographs develops up like that shewn in the lantern slide in which the top spectrum is of tin supposed to be pure, the middle is a commercial tin under examination, and the bottom is of lead, the metal whose presence or absence is in question. It will be seen by the presence of the sensitive lines of wavelengths 2614, 2663, 2803 and 2833, not only that the commercial tin contains some lead, but also, as shewn by line 2833, that a trace of lead is present in the supposedly pure metal.

It is not, of course, necessary to adopt this precise arrangement of spectra, but it is one that is very frequently convenient.

If examinations for the presence of other metals require to be made on the same sample, or if other samples are to be tested, the same plate can be used by racking the dark slide to a fresh position, and as many as six strips (that is, eighteen spectra in all), will easily go on a single plate.

An apparatus has been devised for obviating the necessity of taking comparison spectra. I have named it the Spectrum Comparator. One is supposed to possess a number of spectrograms of the ingredients more commonly to be expected. To build up such a collection is easy in any laboratory possessing a spectrograph.

One takes a spectrogram of the sample under test and places it together with that of the looked for ingredient on the spectrum comparator. Enlarged images are by that instrument projected in close juxtaposition on to a screen and a comfortable scrutiny can be made for any lines

common to the two samples, the presence of common lines indicating, of course, the presence in the sample of the metal to which those lines are due.

(2) *To determine the whole of the Metallic Ingredients of a Sample.*

For this purpose a measuring micrometer is required, consisting of a microscope magnifying about twenty times with a traversing movement accurately measurable over a range of about 6 inches. The slide to be examined is placed on the stage and is illuminated from below by a mirror which travels with the microscope.

A set of photographs is taken as described above, the top spectrum being of iron.

The wavelengths of the unknown lines of the sample are then measured by linear interpolation between the known wavelengths of the iron comparison spectrum.

Having found the wavelengths of a few of the unknown lines in this way, reference to wavelength tables will enable the corresponding metals to be identified.

Having determined one or more of the constituents, a second photograph can be taken in which the bottom spectrum is that of the constituents thus found, and further search made for lines still unidentified.

Here I must give a word of warning. The method of simple linear interpolation is in the case of prism spectrographs only applicable over a narrow range. Should there be no reference lines sufficiently close for linear interpolation the Hartmann formula should be used. Information on this point is to be found in the booklet *Spectrum Analysis with Hilger Instruments*, published by Adam Hilger, Ltd.

The Photographic Plates present no difficulty. Most of the well-known makes are quite satisfactory. For metallurgical work I cannot think of any occasion when it is necessary to use colour sensitive plates.

MEASURING WAVELENGTHS, IDENTIFYING METALS BY THEIR EMISSION SPECTRA AND APPLICATIONS OF SPECTRUM ANALYSIS.

Other Aids to Spectrum Analysis.

Modern steels may contain several metals, all of which have highly complex spectra, and in addition a small quantity of impurities, some of which may be of great importance. When in America in 1913, I was speaking on this subject to Dr. Sargent of the Crucible Steel Company, who gave me a piece of steel for analysis. I asked him to pick out, from a printed list of the elements which I had with me, those which he thought could not be present, or if present could not be of interest. He left me with a list of about fifty elements, any one of which might, he thought, be present, and any one of which might be of importance.

To measure wavelengths of the unknown lines, in such complex spectra, it is necessary to have the wavelengths of a large number of known lines throughout the spectrum. These must be easily reproducible in the laboratory, and must be known with an accuracy beyond question. A sufficient number of lines of the iron spectrum have now been standardized and approved by an International Committee.

Slide 16 shews some of the international standards of wavelength, which as you see are given with enormous accuracy.

Tables of another kind are also necessary, giving the wavelengths of distinctive lines of the elements. These need not be of a like accuracy with the reference lines, and they are available for all the metals, but until the last couple of years they were scattered throughout a number of publications, of which a complete collection was not only very costly, but very confusing and very cumbrous. It was the last step in the work I have been doing for the last twenty years to prepare a little compilation which I have called "Wavelength Tables for Spectrum Analysis," which contains, in one very small volume, all the tables that are necessary for qualitative analysis though for convenience one may add to it a set of enlarged photographs of the iron arc spectrum marked with wavelengths. (Slide 17.) This last saves the trouble of referring to the

tables of standard iron reference lines. The tables are also useful in quantitative analysis, though at this date they can be supplemented by information more recently available.

I might here point out that in every spectrum there are groups of lines which are highly characteristic of the metal, and these become familiar and recognisable at a glance by those making frequent use of the spectro-

The following Iron secondaries were all formally adopted by the International Solar Union in 1910 and 1913. The tertiaries and Neon secondaries are recommendations of the "Commission des étalons de longueur d'onde et tables de spectres solaires" at the meeting of the International Astronomical Union in Rome, May, 1922. They are all in I. A.

The letter "R" signifies that the line is reversed, "r" that it is shaded or diffuse on the red side.

SECONDARIES AND TERTIARIES BETWEEN
λ3370 AND λ6750

IRON LINES.			IRON LINES.		
Secondary Standards.	Tertiaries Interpolated.	Intensity.	Secondary Standards.	Tertiaries Interpolated.	Intensity.
3370-789	.788	6	3513-821	3506-501	5
	3379-023	4		.821	5
	3380-115	5		3521-265	5r
	3392-657	5		3529-821	4
	3396-981	3		3541-088	6
3399-337	.337	6	3556-881	3542-080	5
	3401-523	4		3545-642	5
	3402-262	4		.881	6
	3407-463	7		3558-519	5r
	3413-136	7		3565-382	6R
	3417-845	6		3576-761	4
	3418-511	5		3581-196	8R

LANTERN SLIDE No. 16.

The above appears in "Wavelength Tables," page 13.

graph. I cannot emphasize too much the great advantage of becoming acquainted with these groups of lines. Only those who have had a little experience can realise with what certainty one can in many cases state at a glance the presence of those metals with whose line groups one has become familiar. You will perhaps realise this better when I ask you to compare the difficulty of identifying a man by cranial and facial measurements compared with the certainty and ease with which one recognises him by a glance at his features as a whole.

		4271.766	
		4294.130	
4282.408		4315.089	
4307.909		4337.052	
4325.766			4352.741
		4369.777	
4367.583		4383.550	
4375.934		4415.128	
4404.754			4422.573
4427.314		4442.346	4454.386
		4461.657	
		4490.088 &	4489.745
		4494.572	
		4523.623	
		4547.853	
4531.155			4592.658
M4556.130		4602.347	
4619.297		4632.318	4611.290B
4630.128		4654.504	4647.439
4667.461		4673.171	
		4691.417	
		4736.786	
		4745.808	
		4789.657	
M4871.330		4859.758	4872.149M
4878.225		4903.325	
B4890.770		4919.007	4920.521
		4966.104	
		5001.881	
		5041.076	
		5049.827 &	.760
M4957.606 &		5083.344	5051.639
		5127.365	5110.415
		5171.601	5152.312B
			5192.363
		5227.123	5194.950B
		5240.852	5232.957
		5240.350	5269.540
		5274.156	5302.215
		5341.028	5328.537
			5364.959B
		5405.780	5397.134
		5434.527	5424.057B
		5455.614	5497.522
		5505.784	
		5569.633	5602.788B
		5615.661	
		5658.836	
		5709.396	
		5763.013	
		6055.492	
		6136.624 &	6137.701
		6219.290	6200.323
		6252.567	
		6277.026	
		6319.013	
		6393.612	
		6430.859	
		6494.993	
		6545.250	
		6592.928	
		6675.004	
6191.568			
6230.734			
6265.145			
6335.341			
6421.362			

TYPICAL APPLICATIONS.

I have now given a brief account of what is necessary for spectrum analysis in the way of instruments, accessories, literature and technique. I have even included a good deal that, while adding to the convenience of the worker, is not actually necessary. You will I am sure like now to know what advantages are offered to those brave enough to acquire so formidable a battery of attack.

I cannot do better than quote a selection of remarks by actual users of spectrographs.

* 1. "First of all, spectroscopy holds the premier position as a means of detecting and identifying minute quantities of the elements. A mere trace, perhaps half a milligram, of a soot-like stain on the lead of an electric lamp was carefully removed, transferred to the electrode of a small copper arc lamp, and, by the spectrum of its incandescent vapours, identified as a mixture of tungsten and iron. Not only was the presence of these elements demonstrated, but simultaneously the absence of most other elements in a proportion greater than one per cent. was signified. This last advantage of the spectrographic method, the demonstration of the absence of other elements, is often of more value than the evidence of traces of impurities." †

2. "A single drop of London tap water on drying down on an electrode and arcing reveals the presence of the sodium, magnesium and calcium it contains, although the total solids do not exceed the fiftieth part of a milligram or the three-thousandth part of a grain." †

3. "In the course of a spectrographic examination of the ashes of several drugs and of the ashes of the tinctures prepared from them (*Yr. Bk. of Pharmacy*, 1914, 361-370), it was discovered that boron was present in all." †

4. "Two glasses were examined and . . . it was learnt that the first contained a notable quantity of zinc, which was not the case with the second." †

* The matter from here to the end is almost all taken from *Spectrum Analysis with Hilger Instruments and Optical Methods in Control and Research Laboratories*, both published by Adam Hilger, Ltd.

† Cantor Lectures, "Recent Applications of the Spectroscope and the Spectrophotometer to Science and Industry," by Samuel Judd Lewis, D.Sc., F.I.C., Ph.C., delivered before the Royal Society of Arts, April 11th, 18th, and 25th, 1921.

5. "The spectrographic method has been successfully applied to the determination of minute quantities of nickel in fats." *

6. Murphy and Lonsdale have found that, for brewery practice, it is not satisfactory to rely on a mere biological analysis of the air in the neighbourhood of foundries, smelting works, etc., and in both water and air analysis use the spectroscope as the only ready means of determining chemical constituents. †

7. Metals (*e.g.* zinc) have been detected in the animal organism by the spectrograph, as, for instance, zinc in the ash of Cobra Venom.

8. The detection of traces of mercury in explosives can be most reliably effected by electrolysing a solution prepared from the explosive, using a platinum wire as electrode, and afterwards exposing the wire to a suitable electric discharge in a vacuum tube, and observing the spectrum by a visual spectroscope. As little as 0.000001 or even 0.0000001 gm. may be detected.

9. "To the analyst the complete qualitative analysis of an unknown alloy, revealed by a spectrogram, is a sure basis for the planning of the most direct and rapid method of attack. As the determination of each element proceeds, the purity of precipitates may be checked as often as desired. The spectrograph proves invaluable in the recognition of impurities, the separation of which would entail a lengthy and difficult procedure, or when the weight of an unknown is less than is necessary to complete the desired determinations. A few hundredths of a gram will usually suffice for spectrographic analysis.

"In the separation of the rarer elements, the spectrograph will show, with precision, the point where each step has been successful. In zinc of certain classes, indium, gallium, and germanium have been isolated in this way; the presence of antimony in lake coppers has been proved; and bismuth has been detected in zinc and in alloys where the presence of a few thousandths of one per cent. would be harmful. An antimony precipitate in a delicate determination may contain a considerable proportion of tin or arsenic, both of which will be revealed. The spectrograph is consequently important to the metallurgist as well as to the analyst.

"Impurities in raw material are often a source of annoyance, especially when their detection involves delay and costly analytical work. Whether

* See footnote on p. 37.

† "Emission Spectrography in Chemical Industry," Samuel Judd Lewis, D.Sc., F.I.C., Ph.C., *Journ. Soc. Chem. Ind.*, June 30th, 1916.

low conductivity in copper is due to arsenic, nickel, or something else, may be quickly found out. Residual traces of boron, magnesium, manganese, silicon, vanadium, and other deoxidising agents are easily identified where wet analysis may fail to reveal their presence, even after days of effort. Complex alloys of any kind are dissociated by the spectrograph into a spectrum, the reading of which gives the elements present, together with an idea of the relative amounts of each. The secrets of the inventors of alloys and hardened metals are no great problems when, for their solution, one can depend on the application of the microscope and spectrograph." *

10. Iron and steel analysis and manufacture are subject to great help from spectroscopic investigation. The detection of traces of metals other than those usually assayed is frequently a matter of practical interest, while the spectrograph has also demonstrated the volatilisation of various metals such as zinc, bismuth, tin, copper, lead, etc., from molten iron.

Further applications of the use of the spectrograph may be cited, as for example, checking the purity of materials used for Atomic weight analysis (*Jour. Chem. Soc.*, Vol. 37, p. 116.) In the Autumn Lecture to the Institute of Metals delivered at the Liège meeting in 1926 by Dr. Rosenhain, the view is put forward that in the scientific investigation of alloys it is necessary to secure materials of the highest possible degree of purity. The spectrograph, on account of its great sensitivity and the speed at which metallic impurities can be detected, is invaluable in this connection.

Although the non-metals are, generally speaking, not very suitable for detection by spectroscopic means, there are occasional instances forming useful exceptions to this general statement. For instance, the detection of fluorine in glass is a problem presenting difficulties by ordinary chemical means. If, however, the powdered glass be mixed with calcium, and the mixture put into the carbon arc, the spectrum shows the distinctive calcium fluoride bands.

A quantitative method developed by Hill and Luckey, depends on a difference in volatility in the constituents of an alloy. They use the arc discharge, and measure the time required for a line to disappear when a given weight of the unknown mixture is burned in the crater of the arc. A visual spectrometer is, of course, used. This method is obviously limited in its application, but in the instance of lead in copper, a range of .004

* "Spectrum Analysis in an Industrial Laboratory," W. H. Bassett and C. H. Davis, *Trans. Amer. Inst. of Mining and Metallurgical Engineers*, read Feb. 1922.

to .216 per cent. can be estimated with all the precision required in refinery work.

At a discussion of the above paper, M. G. Lloyd of the Bureau of Standards, Washington, stated that a spectrographic method of quantitative analysis was in use at the Bureau for determining the impurities in tin boiler plugs, and that when the impurity does not amount to more than 0.1 per cent. the results are quite as reliable as those obtained by chemical analysis. He adds: "Quantitative spectroscopic analyses of steel have been made, especially for the determination of chromium and titanium. For such elements as niobium and molybdenum the spectroscopic estimation of small quantities is more reliable than chemical analysis." *

Mottram also adopted the principle of correlating quantity with the time required for given spectrum lines to disappear, in determining the alkali metals in animal tissues and blood, 0.0000002 gm. of potassium in 0.02 c.c. of solution being a working quantity.

These illustrations are from various publications by users of spectrographs. I will add a few general remarks for which I am indebted to Dr. Samuel Judd Lewis, a well-known worker in this field, to whom many of the above applications are due.

Most problems with which the chemist is confronted are amenable to spectrum analysis. While the usual chemical methods suffice for the majority of these, numerous others arise which are almost or quite intractable by the usual chemical tests; and these may, as a rule, be readily solved spectrographically. Among such are those relating to unsuspected elements and to small quantities.

The spectrograph does not discriminate between that which is looked for and that which is wholly out of mind. For example, few would suspect the presence of chromium in a water, yet it is an occasional, although rare constituent of a natural water. Its proportion is always minute, and it would never be found by chemical means unless specially and laboriously sought in a large quantity of material. Using only a few milligrams of the total solids left on evaporation and examining the residue, by means of the spectrograph its presence is revealed without special effort and without anticipation.

The same applies to metallurgical inquiries. Traces of unsuspected

* Further applications of quantitative spectrum analysis as practised at the Bureau of Standards are given in Scientific Paper No. 444 of the Bureau of Standards (July 1922). The examples given relate to the quantitative estimation of impurities in tin, gold and platinum.

elements which modify the properties of an alloy are detected, often where chemical investigation has failed, and where it is very unlikely to succeed, except on adopting a long and tedious separation from a large quantity.

Another application is the complete analysis when only a very small quantity of material is available. Ten milligrams is usually ample, but complete analysis, including all elements occurring to the extent of one per cent. or more, can usually be made with a fraction of a milligram, while the ten-thousandth of a milligram or less of lead and certain other elements will suffice for full indications, however complex the material which carries it.

Doubt enshrouds many conclusions drawn from chemical tests. The brown colouration of a solution produced by sulphuretted hydrogen is open to various interpretations. A little of the original solution or the solution including the sulphide may be evaporated in a silica basin and transferred to the electrode of a suitable arc lamp, and the element, possibly the elements, responsible for the colouration identified beyond all doubt; for the principal lines for lead, copper, bismuth, tin, etc. have wavelengths far removed from one another and cannot possibly be confused.

Occasionally care is necessary in the identification of lines. For example, the ultimate ray (or principal line) of magnesium has a wavelength of 2852.1, while sodium has a line at 2852.8. This sodium line does not appear unless the more important sodium lines are in strong evidence. Therefore the line may be safely attributed to magnesium if any other magnesium line appears, or if sodium is not in good evidence elsewhere.

Another case is that of barium and caesium, which is illustrated in the following quotation.

"An ore was examined with a view to ascertaining the presence of rubidium and caesium. The direct spectrum of the whole ore revealed the presence of rubidium. Caesium was indicated by a single faint line, and that line was its most persistent line. If the wavelength of this had been determined with very great care, it would have been conclusive evidence. However, such precision is not always convenient, and it happens that the most persistent line of barium has nearly the same wavelength as has that of caesium (Ba 4554.2, Cs 4555.4), and so it was desirable to obtain some decisive distinction. This was done by chemical separation into the alkali and alkaline earth groups, using a trace of sulphate, and subsequent spectrography. The spectrum of the alkaline earth group revealed not only the most persistent line for barium,

but also that at 4934·2, while the spectrum of the alkali group showed that caesium was absent ; only a ghost of a line indicative of barium being seen, which was indeed evidence of the slight solubility of barium sulphate.” *

A third instance is the doublet of sodium at 3302·96 and 3302·35 and the doublet of zinc at 3302·91 and 3302·56, all of about the same intensity. Difficulty is very rarely experienced, however, because neither will appear unless the stronger lines for sodium at 5896, or for zinc at 4811 and 4722 take precedence. Suppose, however, that only this region of the spectrum were available ; there is another zinc line of similar intensity at 3345. If this line also is present, the line in question may be attributed to zinc only, if the two lines are about equal in intensity. But if the other zinc line is not there, the line may be attributed to sodium. The presence of sodium is indicated also if the line is much stronger than the zinc line at 3345.

It is rarely, however, that one is left with no more than the evidence of a single line. The most notable exception is lithium at 6707·87 when present in traces only. If it is accompanied by calcium in quantity, the line should be confirmed directly by comparison with a lithium spectrum, and indirectly by comparison with a calcium spectrum, observing that the line in question is of slightly shorter wavelength than the calcium line at 6717·73. There is also a calcium line at 6707·95.

The chemical detection of small quantities of nickel vanadium or molybdenum in a steel, of zinc or lead in approximately pure copper, or of traces of strontium, barium or magnesium in an “ A.R.” calcium salt, is a long and tedious process, requiring close attention to detail of chemical and physical conditions affecting the progress of separation, any deviation from which may lead to error. Such problems are involved in no uncertainty in spectrographic analysis. The whole substance is disintegrated into its elements under the powerful influence of the arc or spark, and each element is excited so as to emit rays of characteristic wavelength.

The following instance also illustrates the value of spectrography. A stain about the size of a sixpence on a piece of deep-dyed cloth had to be identified. It was not known whether it was organic or inorganic, and the quantity was too small to allow of trial tests. Half of the material might be devoted to ascertaining the presence of lead by removing organic

* Cantor Lectures on *Recent Applications of the Spectroscope and the Spectrophotometer to Science and Industry*, 1921, by S. Judd-Lewis, D.Sc., F.I.C.

matter by extraction or ignition, purifying the inorganic residue, treating with hydrogen sulphide to discover the metal causing a black or brown precipitate, or perchance a colouration only, and applying tests for two or three *selected* elements to the miniature very dilute filtrate, with the possibility, and even the probability, of missing the right ones. All this trouble and uncertainty were avoided by submitting one fourth part of the stain to spectrographic analysis, whereby lead, chromium and barium, were discovered. Not only were these elements found, but the spectrum showed also that all other significant metals were absent ; traces of the elements composing the mineral matter of the cloth were also detected. Three parts of the stain remained for examining the organic components.

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